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The thesis deals with the complex problem of corrosion, scaling and bio-fouling, encountered in many industries using large quantities of water for cooling of heat exchangers.

Chapter-1 gives the economics and importance of corrosion, various forms of corrosion, classification of metals according to their resistance to different industrial chemicals and protective methods for mitigation of corrosion, based on either the modification of the metal or the modification of the corrosive environment. This chapter also deals with the associated problems viz. scaling and fouling experienced in cooling system. The nature of deposits formed and the problems created by these deposits have been described. The microbiological problems particularly those caused by sulphate reducing bacteria have been pointed out, specially the corrosion by hydrogen sulphide produced as a result of the growth of the bacteria. The possibility of abatement of fouling by the use of biocides has been pointed out.

Chapter-2 contains detailed literature survey of the problems of cooling water and methods of reduction of corrosion, scaling and microbiological growth by proper treatments. This chapter provides information on various types of water used for cooling, the types of cooling system e.g. closed, once-through and open-recirculating cooling circuits and the chemical additives e.g. inhibitors, dispersants, defoamers, biocides, antioxidants, pH-stabilizers, sequestrants that are either necessary or not needed in each type of cooling system. The purpose of treatment of water has been brought out and the mechanism of scale formation, the prediction of scaling tendency of water and treatments to prevent scale have been described. The permissible corrosion rates of different metals in cooling systems have been given.
The effect of water velocity and heat transfer rate on scaling has been mentioned. The susceptibility of metals to different forms of corrosion in different types of cooling system has been mentioned. Methods of corrosion control by the use of inhibitors e.g. chromates, phosphates and their combinations have been described. The growth of algae, bacteria in cooling water and their control by the use of algacides and bactericides have been described. The chemicals used are chlorine, chlorinated phenols, quaternary ammonium compounds. Finally the specifications for ideal cooling water have been given for different types of cooling systems. The literature survey also considers the problem of effluent disposal and water conservation.

The research work carried out by the candidate has been described under four different sections e.g. Material & Methods used (Chapter-3), Scale Formation and its Control (Chapter-4.1), Corrosion and its Prevention (Chapter-4.2) and Microbiological Corrosion and its Abatement (Chapter-4.3).

In Chapter-3 the quality of chemicals used, the sources of water tested, methods of chemical analysis of water have been given. It also included the surface preparation of metals for corrosion study, methods of electro-chemical measurements e.g. electrode potential and polarisation of metal in treated and untreated water. Full details of the methods of determination scaling tendency of water, carried out in specially developed 'Beaker Test' and Immersion Heater Test', have been given. The methods of calculation of the scale formed and the efficacy of inhibition of scale have been shown by giving a typical result. The two common indices e.g. Langelier and Ryznar indices, based on the degree of calcium carbonate saturation of the waters, have been described. Certain factors affecting the 'Marble Test' for
pHs determination, as required for the calculation of the above mentioned indices, have been investigated and modified. Details of microbiological study e.g. preparation of Baars' media, inoculation of the media with standard sulphate-reducing bacteria, method of sterilization and determination of corrosion in presence of bacteria as well as inhibition by biocides have been described. Methods of determination of polarisation in the presence of anaerobic bacteria have been provided.

Chapter-4.1 deals with the mechanism of scale formation by untreated and treated water and methods of reduction of scale by pH modification and use of inhibitors. Two test methods e.g. 'Beaker Test' and 'Immersion Heater Test' were used. In the Immersion Heater Test three litres water was boiled down to 2500 c.c. In the beaker test 100 c.c. of water was boiled down to half of its volume in a beaker. The original volume was again made up with the same water and again it was boiled down to half of its original volume. This was repeated 5 times in which the total volume of water used was 350 c.c. Finally the adherent scale was washed, dried and weighed. The beaker test provided the value of only adherent scale while the Immersion Heater Test provided the values of total scale precipitated as also the amounts of adherent and non-adherent scale by analysis of samples of filtered water and acidified water at the end of the test. The experimental results have been given separately as obtained in each of the above mentioned test methods. Result obtained in the Immersion Heater Test was found to be reproducible. The total scale precipitated was approximately 30% of the total scale-forming ions present in the quantity of water (3000 ml.) used in this test. The total scale was about 75% of the carbonate (temporary) hardness forming ions. Very little of
the ions (chlorides and sulphates of Ca and Mg) responsible for permanent hardness were precipitated since the water was not concentrated to an extent which would result in the supersaturation of the solution with respect to these ions, which are highly soluble (solubility of CaSO$_4$ - 1250 mg/l, MgSO$_4$ - 170,000 to 356,000 mg/l). About 95% of the mass of the total scale consists of calcium salts and only little magnesium, this being due to the lower solubility (15-13 mg/l) of CaCO$_3$ as against higher solubility (85 mg/l) of MgCO$_3$.

In untreated water the adherent and non-adherent scale were found to be approximately 54 & 46% of the total scale precipitated. In diluted untreated water both types of scale formed were in proportion to the extent of dilution. The number of cycles as well as longer test duration had only slight and insignificant effect on the percentage of total scale precipitated but the nature of the scale was substantially modified; the adherent scale was increased with corresponding decrease in the non-adherent scale. The use of larger quantity of water resulted in the formation of larger mass of scale as also increased percentage of scale, calculated as % of the scale forming ions. The adherent scale was also considerably increased. Certain cations representative of those responsible for permanent hardness of water were introduced to determine their effects. In the presence of magnesium sulphate the total scale was considerably decreased possibly owing to the greater solubility of calcium carbonate in presence of added magnesium sulphate. Calcium sulphate did not produce any change in total scale but had some effect on the nature of scale. Introduction of sodium chloride in the water caused considerable reduction of total scales (16% instead of 31% of total scale-forming ions). The nature of scale was also changed, the adherent scale reducing to 33% of the total scale as against 54%
in untreated water.

Reduction of scaling tendency of water by modification of pH was studied in detail. For this the pH of a hard water was progressively reduced by different amounts of acid and the scale formed by the treated waters was determined. The changes in L.I., Ryznar and methyl orange alkalinity, as a result of acidification were noted. It was found that on acidification there was progressive reduction in total scale, including adherent and non-adherent scale. Scale formed at pH 6.55 & 6.0 was 17.7 & 3.95% of the total scale forming ions respectively as against 30.8% in untreated water at pH 7.1. At 6.55 pH, the inhibition of adherent & non-adherent scale was 6.1 and 85.0% respectively. At 6.0 pH the inhibition of adherent and non-adherent scale was 100 and 71% respectively. The use of acid (sulphuric acid) converts the sparingly soluble calcium carbonate and magnesium carbonate to their highly soluble salts e.g. CaSO₄, MgSO₄ accounting for the reduction of scale.

Different types of acids e.g. H₂SO₄, HCl and chromic acid were used for pH modification and it was found that in every case there was reduction in scale with lowering of pH. While scale was reduced at lower pH, the corrosive tendency of water was increased depending on the nature of salt formed with the acids used. It was found that out of all the acids examined, chromic acid was superior since it acted not only as reducer of the scaling property of water but also due to its content of hexavalent chromium it proved to be a corrosion inhibitor.

A number of anti-scalant and anti-corrosive additives were used to determine their scale-inhibitive effect. Cutting oil increased adherent
scale. Addition of hexa-metaphosphate (2 ppm) resulted in some inhibition of total scale and greater inhibition of the adherent scale (60%). The reversion of hexametaphosphate to orthophosphate which forms loose sludge with calcium and magnesium salts is responsible for the lowering of the inhibition of the total as well as the non-adherent scale. However, it modifies the precipitated calcium salts so that they become less adherent.

The findings of the immersion heater test were confirmed by the 'Beaker Test' and the results obtained were generally similar to those obtained in the former test. For example, there was progressive reduction of adherent scale with lowering of pH. The mechanism of reduction of scale with lowering of pH was studied in detail by the determination of pH, total hardness and methyl orange alkalinity after addition of different quantities of acid. The changes in these values after the treated water were kept in contact with CaCO₃ were also determined. The latter gave the CaCO₃ saturation values of pHs, and the so called THs and MOs. The Langelier Index and Ryznar values were changed and the amounts of scale were closely related to those predictable by the Langelier and Ryznar indices. The loss or uptake of CaCO₃ directly determined quantitatively when the water was kept in contact with CaCO₃, could also explain the scaling behaviour of the treated waters.

Out of the three acids examined e.g. sulphuric acid, hydrochloric and chromic acid, best result from the point of view of both scale reduction and corrosion inhibition was provided by chromic acid.

Certain additives e.g. "Calgon" and tannin were used for scale control. Calgon (10 ppm) reduced the adherent scale by 60% and tannin
afforded 90% protection at optimum concentration (100 ppm).

Organophosphonates were tested for their anti-scalant properties. Scaling tendency was considerably reduced in their presence. Organophosphonates also inhibit the precipitation of calcium salts in a mixture of two incompatible solutions containing \( \text{CaCl}_2 \) and \( \text{NaHCO}_3 \).

Correlation between the scaling property of various natural waters and the different parameters of the water e.g. hardness, total solids, Langelier and Ryznar indices etc. was sought. It was found that no correlation could be obtained due to the wide variation not only in the amounts but the nature of scale forming ions present in the water. One of the reasons for the lack of correlation between the scale and Langelier and Ryznar indices is due to the drawback of the indices which treat the problem of protective calcium film formation in terms of solution chemistry overlooking the importance of electro-chemical reactions during the corrosion of metal in water, which produces considerable amount of alkalies by the cathodic reduction of oxygen. However, it was found that there was excellent correlation between the scale formed and the values of Langelier and Ryznar indices, methyl orange alkalinity and uptake or loss of calcium carbonate in such waters wherein the relative contents of the calcium and magnesium salts and the carbonate and non-carbonate hardness values were nearly constant. For example, good correlation was obtained in waters treated with acids or alkalies or where the water was diluted since these treatments did not affect the relative concentrations of the cations.

Chapter-4.2 deals with the methods of corrosion control in cooling water. In the first instance the conditioning of water by alkali treatment was studied to determine its effects. In its presence it was found
that not only the natural waters but specially prepared aggressive waters could be rendered non-corrosive by alkali treatment. The treatment increased the pH values which resulted in the crystallisation of calcium to form protective film. This was confirmed by the values of Langelier and Ryznar indices and changes in the methylorange alkalinity and total hardness values as a result of contact with calcium carbonate. However, the treatment should be carefully done so that only a thin protective scale (not excessive) is deposited.

The addition of chromate was found to be very useful as a corrosion inhibitor even in water containing an electrolyte (Na₂SO₄). In the presence of optimum concentration of chromate the test coupons remained completely free from corrosion and the potential of the steel panels were considerably ennobled, proving increased anodic polarisation of steel by chromate.

Various combinations of chromate, phosphate and zinc were tested for their anticorrosive effects. A number of combinations proved satisfactory and showed synergistic effect, in that they afforded better protection than those expected from their individual effects. Examples of excellent inhibition (complete protection) are provided by 250 ppm chromate plus 20 ppm phosphate, 100 ppm chromate plus 20 ppm phosphate plus one ppm zinc. It may be stated that zinc or phosphate alone is unable to protect steel.

Organophosphonates, besides being useful descaler, also proved to be a fairly effective corrosion inhibitor. The inhibition by phosphonates was augmented by the presence of traces of zinc ions.

In the presence of combinations containing phosphonates in water containing electrolyte the values of electrode potentials of mild steel were nobler than in inhibited water with or without zinc.
Polarisation measurements clearly demonstrated the anodic nature of chromate. It considerably increased the anodic polarisation without much effect on cathodic polarisation. The anodic polarisation was also increased in presence of zinc. Zinc affected the cathodic polarisation. The superior performance of combination of chromate with zinc is attributed to anodic polarisation by chromate fortified by cathodic polarisation by zinc ion.

Factors responsible for the depletion of chromate was studied. The presence of active metal e.g. iron promoted greater depletion which also depended on the area of the metal surface kept in contact with water. The depletion of chromate was in the following decreasing order when in contact with the metals tested:- Fe, S.S., Cu, Brass.

Industrial cooling systems are also subjected to bio-fouling which are deposited on heat exchanger surfaces and substantially impair heat transfer co-efficient. The common fouling micro-organisms are algae & sulphate-reducing bacteria (SRB). Algae can be controlled by the use of chlorine, applied preferably by shock dosing for a few hours each day.

Control of algae has been satisfactorily practiced in the industry, but less attention has been paid to control of sulphate-reducing bacteria. These bacteria thrive in anaerobic conditions at places favouring their growth e.g. cooling tower basins, under deposits of scale and tubercles formed inside water pipes.

Sulphate reducing bacteria produces H₂S in their metabolic process which in turn, causes attack on iron and other metals. The iron sulphide formed produces further corrosion.
Studies were, therefore, made (described in Chapter-4.3) to ascertain if some anti-bacterial chemicals would be effective in controlling the growth of SRB and inhibit the corrosion caused by it. Potassium chromate, sodium pentachlorophanate, sodium trichlorophanate & tannin were tested. The following chemicals proved to be toxic for SRB in Baar's media: Chromate and Sodium pentachlorophanate. Near complete inhibition of bacterial growth and corrosion was achieved by the use of 150 ppm of potassium chromate and 200 ppm of sodium pentachlorophanate.

The inhibitive effect of some of the chemicals were also studied by polarisation measurements to get insight into the mechanism of inhibition. The chemicals studied were potassium chromate, tannin, sodium trichlorophenol & sodium pentachlorophenol.

Chromate polarised the anode considerably. Tannin, sodium trichlorophenol & sodium pentachlorophenol suppressed bacterial activity by polarising cathodic reaction.

It has been proved that the complex and interconnected problems of corrosion, scaling and microbiological fouling can be controlled by the use of judicious pH control, and by the addition of mixtures of chromate, zinc, organophosphonate, sodium hexametaphosphate and sodium pentachlorophanate.